# Electronic structure and optical properties of $[(ZnSe)_m(CdSe)_n]_N$-ZnSe multiple quantum wells

Shang-Fen Ren*
*National Laboratory for Superlattices and Microstructure, Institute of Semiconductors, Chinese Academy of Science, P.O. Box 912, Beijing 10083, China*
*and Department of Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801*

Jian-Bai Xia
*National Laboratory for Superlattices and Microstructure, Institute of Semiconductors, Chinese Academy of Science, P.O. Box 912, Beijing 10083, China*
*and Chinese Center of Advanced Science and Technology (World Laboratory), Beijing, China*

He-Xiang Han and Zhao-Ping Wang
*National Laboratory for Superlattices and Microstructure, Institute of Semiconductors, Chinese Academy of Science, P.O. Box 912, Beijing 10083, China*
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The electronic energy bands of $(ZnSe)_m(CdSe)_1$ and $(ZnSe)_{m-1}(Cd_{0.5}Zn_{0.5}Se)_2$ ($m = 2, 3$) superlattices are calculated with the empirical nonlocal pseudopotential method taking into account the strain effect. The energy gaps, effective masses along different directions, the splitting of heavy- and light-hole bands, and spin-orbit splitting, etc. are obtained. Assuming that the $(ZnSe)_2(CdSe)_1$ and $(ZnSe)_3(CdSe)_1$ superlattices in the corresponding $[(ZnSe)_m(CdSe)_n]_N$-ZnSe ($m = 2$ or 3, $n = 1$) multiple quantum wells as a whole are one kind of potential-well materials, we calculated the quantum energy levels of the electron and the heavy hole, and the exciton binding energies as functions of period number $N$ of the superlattice. The variations of energy gaps of the two superlattices with temperature are calculated. Taking into account the confined energy in the quantum well and the exciton binding energy, the energy positions of exciton peaks are compared with the luminescence experiments of the multiple quantum wells. The variations with temperature are in good agreement, and the discrepancies between the calculated results and the experimental data are suggested as being due to the interface alloy formation.

Recently blue and green lasers have been successfully fabricated with ZnSe-based $ZnSe/Zn_{1-x}Cd_xSe$ superlattices,[1-3] which has caused intense interest in research on superlattices of II-VI compound semiconductors. Because the difference between the lattice constants of ZnSe and CdSe is large (about 7%), there is large strain in the ZnSe/CdSe quantum wells or superlattices. The research shows that the critical thickness of the pure ZnSe/CdSe well is only several monolayers of atoms, so the adjustable range of the optical energy gap of the ZnSe/CdSe quantum well is extremely limited. In order to overcome this difficulty, $[(ZnSe)_m(CdSe)_n]_N$-ZnSe multiple quantum well structures composed of $(ZnSe)_m(CdSe)_n$ short-period superlattices and the barrier material ZnSe have been proposed,[4] as shown in Fig. 1(a). This kind of structure can increase the critical thickness of the ZnSe/CdSe superlattice growth and give a larger adjustable range of the optical energy gap.

In this paper we studied the electronic structures of $[(ZnSe)_m(CdSe)_n]_N$-ZnSe multiple quantum wells and their optical properties. First we calculated the electronic structures of the $(ZnSe)_m(CdSe)_1$ short-period superlattices ($m$=2,3) with the empirical nonlocal pseudopotential method,[5] and obtained energy gaps, effective masses along different directions, splitting of heavy- and light-hole bands, and spin-orbital splitting, etc. Because the number of ZnSe monolayers $m$, in the superlattices is so small, the quantum confined effect is not strong; hence the superlattice can be treated as a kind of potential-well material with ZnSe thick potential barrier layers on both sides. In this approximation we calculated the electronic and hole energy levels in wide-well confinement and the corresponding exciton binding energies. We also calcu-

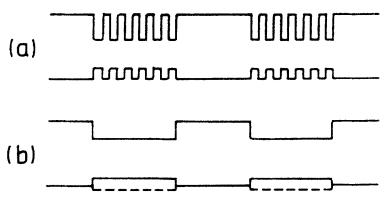


FIG. 1. Schematic figure of energy bands of $[(ZnSe)_m(CdSe)_n]_N$-ZnSe multiple quantum well structures. (a) Precise energy band. (b) Energy band in the effective-mass approximation; dashed line is that of the light hole.

 

TABLE I. Energy gaps and splitting at Γ point (in eV), and effective masses (in $m_e$) in $(ZnSe)_m(CdSe)_1$ and $(ZnSe)_{m-1}(Cd_{0.5}Zn_{0.5}Se)_2$ $(m = 2, 3)$ superlattices.

| | Energy gap | Dir. | $m_e$ | $m_{hh}$ | $m_{lh}$ | $m_{sp}$[a] |
|---|---|---|---|---|---|---|
| $(ZnSe)_3(CdSe)_1$ | $E_g$=2.368 | [001] | 0.160 | 1.278 | 0.405 | 0.406 |
| $a_\parallel = 5.668$ Å | $\Delta_0 = 0.526$ | [100] | 0.164 | 0.294 | 0.368 | 1.067 |
| $a_\perp = 5.881i$ Å | $\Delta_{hl} = 0.135$ | [110] | 0.166 | 0.271 | 0.438 | 1.165 |
| $(ZnSe)_2(CdSe)_1$ | $E_g$=2.282 | [001] | 0.163 | 1.374 | 0.491 | 0.219 |
| $a_\parallel = 5.668$ Å | $\Delta_0 = 0.605$ | [100] | 0.163 | 0.286 | 0.338 | 1.000 |
| $a_\perp = 5.952$ Å | $\Delta_{hl} = 0.156$ | [110] | 0.165 | 0.286 | 0.353 | 1.009 |
| $(ZnSe)_2(Cd_{0.5}Zn_{0.5}Se)_2$ | $E_g$=2.467 | [001] | 0.161 | 1.240 | 0.356 | 0.269 |
| $a_\parallel = 5.668$ Å | $\Delta_0 = 0.527$ | [100] | 0.164 | 0.292 | 0.386 | 0.697 |
| $a_\perp = 5.880$ Å | $\Delta_{hl} = 0.125$ | [110] | 0.167 | 0.344 | 0.338 | 0.665 |
| $(ZnSe)_1(Cd_{0.5}Zn_{0.5}Se)_2$ | $E_g$=2.409 | [001] | 0.160 | 1.248 | 0.422 | 0.222 |
| $a_\parallel = 5.668$ Å | $\Delta_0 = 0.577$ | [100] | 0.164 | 0.291 | 0.356 | 0.727 |
| $a_\perp = 5.950$ Å | $\Delta_{hl} = 0.149$ | [110] | 0.167 | 0.343 | 0.313 | 0.698 |

[a] $m_{sp}$ is the effective mass of the spin-orbital splitting band.

lated the shift of exciton peak energy induced by the temperature effect, and compared it with photoluminescence experiments.

To take into account the strain effect we used an empirical pseudopotential of atomic type,[5] in which the local part is given by

$$V_L = v_1 e^{-\alpha_1 r^2} + v_2 r^2 e^{-\alpha_1 r^2} + v_3 e^{-\alpha_3 r^2}, \quad (1)$$

where $v_1, v_2, v_3$ are adjustable parameters, and $\alpha_1$ and $\alpha_3$ are fixed for anions and cations. The nonlocal potentials take the form

$$V_{NL} = \sum_{lm} A_l e^{-(r/R_c)^2} |lm\rangle\langle lm|, \quad (2)$$

where $|lm\rangle$ is the eigenfunction of angular momentum with quantum number $l$, $m$, $A_l$ are adjustable parameters, and $R_c$ is the core radius fixed at 2.3 a.u. The spin-orbit coupling potential is

$$V_{SO} = \lambda \sum_{b,b'} |b\rangle\langle b|\vec{\sigma}\cdot\vec{L}|b'\rangle\langle b'|, \quad (3)$$

where $\vec{\sigma}$ and $\vec{L}$ are the Pauli matrix and the angular momentum operator, respectively. $\langle\vec{r}|b\rangle = \{x, y, z\}e^{-(r/R_c)^2}/\sqrt{S}$ denote three effective $p$-like core orbitals, $S$ being the normalization constant. The parameters for both CdSe and ZnSe at room temperature are taken from Ref. 5.

In the ZnSe-based ZnSe/CdSe superlattices the strain occurs in the CdSe layer. Due to the elastic energy the lattice constant of CdSe in the growth direction is 6.521 Å; in the direction parallel to the interface the lattice constant is the same as that of ZnSe, 5.668 Å. The band offset of the ZnSe/CdSe hetro-interface is calculated as 0.331 eV by using the first-principles pseudopotential calculations.[5] Taking into account the strain effect and the spin-orbital splitting of the valence band, we calculated the energy bands of $(ZnSe)_m(CdSe)_1$ $(m$=2,3) short-period superlattices. Both superlattices have direct energy gaps, the effective mass of the electron and heavy and light holes along different directions can be determined from the form of the energy band near the Γ point. The energy band parameters and the effective mass for these two superlattices are listed in Table I (the

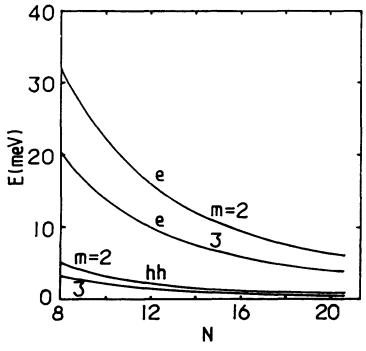


FIG. 2. Ground state energy of electron and heavy hole in the $[(ZnSe)_m(CdSe)_1]_N$-ZnSe multiple quantum wells as functions of superlattice period $N$.

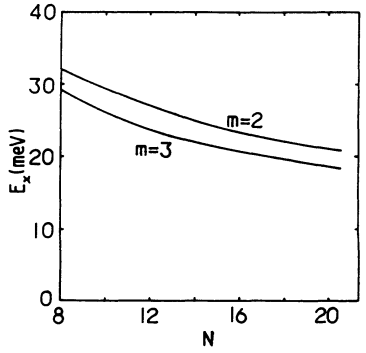


FIG. 3. Exciton binding energy in the $[(ZnSe)_m(CdSe)_1]_N$-ZnSe multiple quantum wells as function of superlattice period $N$.

numbers for the two alloy superlattices will be explained later).

In $[(ZnSe)_m(CdSe)_n]_N$-ZnSe multiple quantum well structures, the $(ZnSe)_m(CdSe)_1$ ($m$=2 or 3) superlattices can be treated as a material (digital alloy) which becomes a potential well between the ZnSe potential barriers, as shown in Fig. 1(b). Due to the strain existing in the superlattices there is a splitting between heavy- and light-hole bands $\Delta_{hl}$ (see Table I); the light-hole energy level will be lower than that of ZnSe, as shown by the dashed line in Fig. 1(b). Thus for the light hole the thick ZnSe layer is the potential well.

Because the ZnSe potential barrier is thick (about 130 Å), we assume that the coupling between neighboring wells can be neglected and calculate the quantum states in a single quantum well. Taking the ratio of conduction and valence band offset as 0.65:0.35,[5] we calculated electronic and heavy-hole ground state energy levels in the $[(ZnSe)_m(CdSe)_1]_N$-ZnSe ($m$=2 or 3) multiple quantum wells as functions of superlattice period number $N$, as shown in Fig. 2. From Fig. 2 we see that due to the ZnSe potential barrier level the electronic and heavy-hole bands of $(ZnSe)_m(CdSe)_1$ superlattices are quantized once again; the energies of the ground states decrease with the superlattice period number $N$, i.e., the width of the quantum well, similar to that of the ordinary quantum well. The period of the $(ZnSe)_2(CdSe)_1$ superlattice is smaller than that of the $(ZnSe)_3(CdSe)_1$ superlattice, hence the confinement energies are larger.

The exciton binding energy in the II-VI semiconductor superlattices is large; therefore in order to compare with experiments we have to consider the exciton effect. We assume that the wave function of the exciton state is

$$\Psi_{ex}(\vec{r}) = \phi(\vec{\rho})\psi_e(z_e)\psi_h(z_h), \tag{4}$$

where $\vec{\rho}$ is the coordinate in the parallel plane, and $\Psi_e, \Psi_h$ are electronic and heavy-hole wave functions in the quantum well, respectively. Inserting Eq. (4) into the exciton Schrödinger equation, we obtain the equation of $\Phi(\vec{\rho})$,

$$\left[-\frac{\hbar^2}{2\mu}\nabla_\rho^2 + V_{\text{eff}}(\vec{\rho})\right]\phi(\vec{\rho}) = E_x\phi(\vec{\rho}), \tag{5}$$

where

$$V_{\text{eff}}(\vec{\rho}) = -\frac{e^2}{\epsilon}\int\int dz_e dz_h \frac{|\psi_e(z_e)|^2|\psi_h(z_h)|^2}{[(z_e-z_h)^2+\rho^2]^{1/2}}, \tag{6}$$

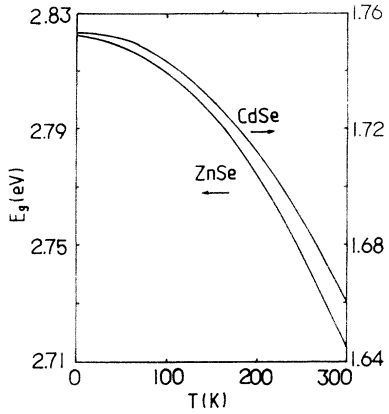


FIG. 4. Energy gaps of ZnSe and CdSe as function of temperature.

$\mu$ is the reduced mass of the electron and heavy hole, and $E_x$ is the exciton binding energy. Expanding $\Phi(\vec{\rho})$ with a group of Gaussian functions,

$$\phi(\vec{\rho}) = \sum_i C_i\sqrt{\frac{2\alpha_i}{\pi}}e^{-\alpha_i\rho^2}, \tag{7}$$

and inserting it into Eq. (5), we obtain the secular equation

$$|H_{ij} - E_x S_{ij}| = 0, \tag{8}$$

where $S_{i,j}$ is the overlap integral of the basis functions and $H_{ij}$ is the Hamiltonian matrix element:

$$S_{ij} = \frac{2\sqrt{\alpha_i\alpha_j}}{\alpha_i} + \alpha_j, \tag{9}$$

$$H_{ij}^0 = \frac{\hbar}{2\mu}\frac{4\alpha_i\alpha_j}{\alpha_i} + \alpha_j S_{ij}, \tag{10}$$

$$H_{ij}^1 = \frac{2e^2}{\epsilon}\sqrt{\frac{\pi\alpha_i\alpha_j}{\alpha_i+\alpha_j}}\int\int dz_e dz_h|\psi_e(z_e)|^2|\psi_h(z_h)|^2 \times \text{erfc}(\sqrt{\alpha_i+\alpha_j}z)e^{(\alpha_i+\alpha_j)z^2}, \tag{11}$$

where $H_{ij}^0, H_{ij}^1$ refer to the kinetic energy and potential energy terms in Eq. (5), respectively, erfc($x$) is the complementary error function, and $z = |z_e - z_h|$. Solving Eq. (8), we obtain binding energies of the electron–heavy-hole exciton in the two multiple quantum well structures

TABLE II. Lattice constants (in Å) and energy gaps (in eV) in $(ZnSe)_m(CdSe)_1$ ($m$ = 2, 3) superlattices at different temperatures (in K).

| | $T$ | 0 | 10 | 60 | 100 | 150 | 200 | 250 | 300 |
|---|---|---|---|---|---|---|---|---|---|
| $(ZnSe)_3(CdSe)_1$ | $a_\parallel$ | 5.6618 | 5.6618 | 5.6621 | 5.6625 | 5.6634 | 5.6646 | 5.6661 | 5.6680 |
| | $a_\perp$ | 5.8748 | 5.8748 | 5.8706 | 5.8755 | 5.8764 | 5.8777 | 5.8793 | 5.8812 |
| | $E_g$ | 2.468 | 2.467 | 2.463 | 2.456 | 2.442 | 2.422 | 2.396 | 2.367 |
| $(ZnSe)_2(CdSe)_1$ | $a_\parallel$ | 5.6618 | 5.6618 | 5.6621 | 5.6625 | 5.6634 | 5.6646 | 5.6661 | 5.6680 |
| | $a_\perp$ | 5.9458 | 5.9458 | 5.9461 | 5.9465 | 5.9474 | 5.9487 | 5.9503 | 5.9523 |
| | $E_g$ | 2.380 | 2.380 | 2.376 | 2.369 | 2.350 | 2.336 | 2.311 | 2.280 |

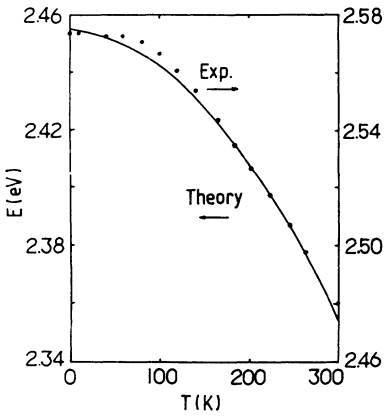


FIG. 5. Experimental and theoretical energies of exciton luminescence peak in the $[(ZnSe)_3(CdSe)_1]_{14}$-ZnSe multiple quantum well at different temperatures. Dots represent experimental values, and the solid curve is theoretical values.

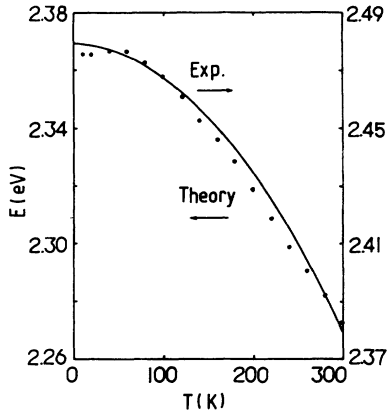


FIG. 6. Same as Fig. 5, but in the $[(ZnSe)_2(CdSe)_1]_{14}$-ZnSe multiple quantum well.

as functions of the superlattice period number $N$; the results are shown in Fig. 3. From Fig. 3 we see that the exciton binding energy decreases with $N$, approaching the limit in the bulk material, 17 meV. Comparing Figs. 2 and 3, we find that the variation of the exciton binding energy with $N$ is not as large as that of the confined energy of the electron in the quantum well. The experimentally measured energy of the exciton peak should be the ground state transition energy minus the exciton energy.

We also considered the temperature effect on the energy gaps of the $(ZnSe)_m(CdSe)_1$ superlattices. First we calculated energy gaps of ZnSe and CdSe single crystals at different temperature, taking into account the variation of the lattice constant with the temperature. One of the pseudopotential parameters $A_{0c}$ is modified to fit the experimental data of the bulk band at different temperatures.[6] The theoretical energy gaps of ZnSe and CdSe are shown in Fig. 4. With the lattice constants and pseudopotential parameters at different temperatures we calculated energy bands of $(ZnSe)_m(CdSe)_1$ ($m$=2,3) superlattices; the lattice constants and energy gaps at different temperatures are given in Table II.

We performed photoluminescence experiments on the $[(ZnSe)_m(CdSe)_1]_{14}$-ZnSe ($m = 2, 3$) multiple quantum well structures, and measured the energies of the exciton peak at different temperatures. The results are shown by dots in Figs. 5 and 6, where the solid curves are theoretical values, which equal the summation of the energy gaps of $(ZnSe)_m(CdSe)_1$ (Table II) and the confined energies of electron and heavy hole (Fig. 2), less the exciton binding energy (Fig. 3) in the quantum well for $N = 14$. From Figs. 5 and 6 we see that the variations with the temperature are in good agreement with experiment. The theoretical values of the exciton peak energy are smaller than the experimental values by 0.11–0.12 eV. We think that the main reason for this discrepancy is the alloy formation at interfaces, which results in increase of energy gaps. We speculate that the samples used in the experiments are actually alloy superlattices, i.e., the $(ZnSe)_3(CdSe)_1$ superlattice is actually the $(ZnSe)_2(Cd_{0.5}Zn_{0.5}Se)_2$ alloy superlattice, and the $(ZnSe)_2(CdSe)_1$ superlattice is actually the $(ZnSe)_1(Cd_{0.5}Zn_{0.5}Se)_2$ alloy superlattice. To prove this, we calculated the energy gaps and effective masses of $(ZnSe)_{m-1}(Cd_{0.5}Zn_{0.5}Se)_2$ ($m = 2, 3$) alloy superlattices, and the results are also listed in Table I. Comparing the results for superlattices with those for their corresponding alloy superlattices, we see that the energy gaps will increase 0.10 eV for the $(ZnSe)_3(CdSe)_1$ superlattice and 0.13 eV for the $(ZnSe)_2(CdSe)_1$ superlattice when alloying occurs at interfaces. Besides the increase of energy gaps, other calculated properties, such as the spin-orbital splitting, heavy-hole–light-hole splitting, and effective masses $m_e, m_{hh}, m_{lh}$ do not change much ($m_{sp}$ change but they are not used in the present calculations). So our calculations of confined energies and the exciton binding energies are still appropriate for alloy superlattices, keeping in mind that the energy gaps of alloy superlattices will increase by about 0.11 eV.

In summary, we calculated energy bands of $(ZnSe)_m(CdSe)_1$ and $(ZnSe)_{m-1}(Cd_{0.5}Zn_{0.5}Se)_2$ superlattices with the empirical nonlocal pseudopotential method taking into account the strain effect. By using the effective-mass envelope function method we calculated the confined energies and exciton binding energies in the $[(ZnSe)_m(CdSe)_1]_N$-ZnSe multiple quantum well structures. The temperature effect on the energy gaps of the $(ZnSe)_m(CdSe)_1$ superlattice is also considered. We measured the energies of exciton luminescence peaks of the $[(ZnSe)_m(CdSe)_1]_{14}$-ZnSe multiple quantum well structures at different temperatures, and compared with our theoretical results. The variation with temperature is in good agreement. The discrepancy between the calculated results and the experimental data is explained by interface alloy formation.

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*Present address: Department of Physics, Illinois State University, Normal, Illinois 61790-4560.

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